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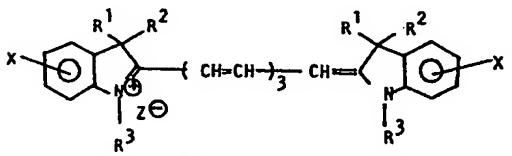
(54) Optical information recording medium.

(57) An optical information recording medium being capable of effecting recording and regeneration by using laser beam which comprises a transparent or opaque substrate and a thin film recording layer, formed on said substrate, said recording layer containing a cyanine coloring matter represented by the following formula:



(wherein, R^1, R^2 and R^3 may be the same or different, each of them stands for an alkyl group having 1 - 6 carbon atoms, X stands for halogen, and Z stands for a superhalogenic ion, a paratoluene sulfonic ion or an alkylsulfuric ion).

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OPTICAL INFORMATION RECORDING MEDIUM

BACKGROUND OF THE INVENTION

a) Field of the Invetion

The present invention relates to a recording medium, in particular relates to an optical information recording medium for use in writing (recording) and reading (regenerating) with a high density energy beam.

b) Description of the Prior Art

A great number of optical information recording mediums for use in writing and reading with a high density energy beam have hitherto been proposed.

As one typical recording medium of such recording mediums, there is enumerated the one which has applied a coloring thin film to the recording layer. The optical memory medium of this type is constructed so that the metal reflective film is formed on the substrate and the coloring thin film recording layer is further formed thereon. When recording information and regenerating it using the medium of this type, it may be done by condensing a laser beam, to which wavelength the recording layer exhibits a maximum rate of light absorption, and radiating such a laser beam from the side of the recording layer of the medium.

Hereupon, said metal reflective film is provided for the purpose of supplementing the deficient amount of the beam reflected form the coloring layer alone. However, the presence of the metal reflective film is defective in that due to this, the structure of the information recording medium becomes complicated and simultaneously the production cost becomes high.

In view of this, an optical information recording medium is

attracting public attention recently, wherein a high-reflective and bronze-lustered organic coloring matter-containing layer is provided directly on the substrate and the metal reflective film is omitted. In particular, when using, as a recording layer, a highly light absorptive cyanine coloring matter and making said recording film have a thickness of 300 Å - 600 Å, there can be obtained a light absorption reflective film which exhibits metal luster (reflective index: 20 - 30%) and permits to effect recording with laser beam and reflective reading with laser beam.

However, the fact is that the cyanine coloring matter-containing recording mediums proposed up to now still involves the following drawbacks: (i) As it is difficult to protect the coloring matter-containing recording layer, information recording or regeneration is likely to be mistaken due to fine dust and the like adhered to the recording layer, (ii) Recording or regenerating sensitivity is not satisfactory, (iii) Preservability can not be kept constant for a long time, and the like.

SUMMARY OF THE INVENTION

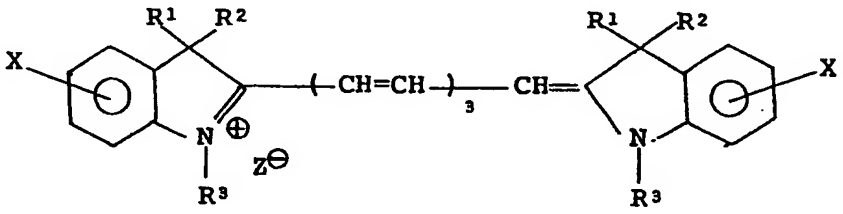
The present invention has been accomplished in the light of the above mentioned problems. The first object of the present invention is to provide an optical information recording medium which is high in both the sensitivity (recording sensitivity and regenerating sensitivity) and the S/N. The second object is to provide an optical information recording medium which is uniform in quality and further superior in preservability (in particular, thermal resistance and light resistance).

The inventors of this application have carried out various studies and investigations in order to achieve the above objects

to find that a compound having a specific structure (a specific cyanine coloring matter) is extraordinally superior in thermal resistance and light resistance among cyanine coloring matters and so is useful for the recording layer. The inventors of this application have carried out further studies and investigations to find that the coexistence of a specific transition metal complex with the above mentioned cyanine coloring matter more improves the stability of the resulting optical information recording medium and furthermore there is no inconvenience to be caused by the coexistence of said transition metal complex.

The present invention has been completed on the bases of this finding.

That is, the present invention relates to an optical information recording medium comprising a substrate and a recording layer (a light absorption reflective layer) formed on said substrate, characterized in that said recording layer is consisted essentially of a cyanine coloring matter represented by the following general furmula I:

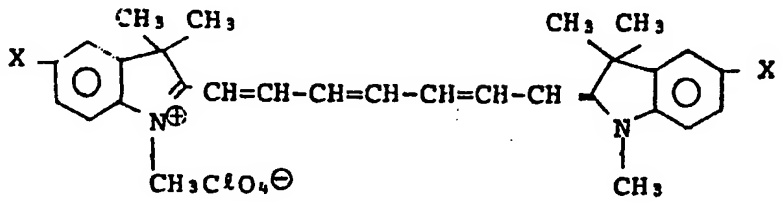


... (I)

(wherein, R^1, R^2 and R^3 may be the same or different, each of them stands for an alkyl group having 1 - 6 carbon atoms, X stands for halogen, and Z stands for a superhalogenic ion, a paratoluene sulfonic ion or an alkylsulfuric ion).

It is particularly profitable to use 1-methyl-2-[7-(1-methyl-3,3-dimethyl-5-halo-2-indolinylidene)-1,3,5-heptatrienyl]-3,3-dimethyl-5-halo-indoliumperchlorate represented by the under

mentioned general formula II from among the cyanine coloring matters represented by the above mentioned general formula I.



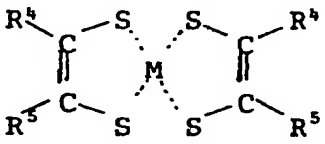
... (II)

(wherein, X stands for a halogen atom selected from the group consisting of fluorine, chlorine, bromine and iodine.) The optical information recording medium according to the present invention is basically consisted of the substrate and the colouring matter thin film (recording layer). Accordingly, the present invention permits the provision of a protective layer on the recording layer, and the provision of an adhesive layer (an undercoat layer) between the recording layer and the substrate respectively as occasion demands. In addition, the present invention permits to adopt the so-called air-sandwich structure wherein a pair of recording mediums, with each recording layer inside, stand face to face through a peripherally provided spacer. The recording layer used for the present invention is suitable to have such a metal-like reflection as the coloring matter displays at a specific light wavelength region, in practice to have a reflection index of 20 % or more, particularly 20 - 40 %, against the wavelength of laser beam used in writing and reading. This reflection is different from said metal-like reflection in that the former has a particular color, but is capable of displaying a high reflection index against the wavelength of laser beam used in recording and regenerating, whereby the amount of light for use in information reading can be increased and the S/N of reading signal can be enhanced.

In this connection, it is to be noted that in case said reflection index is less than 20 %, the signal strength is weak and the signal is apt to be influenced by noises. On the other hand, in case the reflection index is more than 40 % there is a tendency that the absorption light amount decreases and the energy required for recording enlarges.

As described above, it is desirable that the recording layer of the present invention should contain beforehand the specific transition metal complex (namely, the transition metal complex which is more absorbent of the light at the long wavelength range than the coloring matter represented by the above mentioned general formula I).

The transition metal complexes used in the present invention may be those represented by the following structural formula III or their quaternary ammonium salts:



... (III)

(wherein, M is a transition metal selected from the group consisting of nickel, platinum and palladium, R^4 and R^5 may be the same or different, R^4 and R^5 each is an alkyl group, a phenyl group, an alkyl-substituted phenyl group, an alkoxy-substituted phenyl group or a dialkylaminophenyl group or R^4 and R^5 may cooperate to form a ring.).

As the transition metal complexes referred to above there can be enumerated bis(4-diethylaminodithiobenzyl)nickel, bis(4-dimethylaminodithiobenzyl)nickel, bis(3,4,5,6-tetrachloro-1,2-dithiophenyl)nickel tetrabutylammonium, bis(4-chloro-1,2-dithiophenyl)nickel tetrabutylammonium, bis(1,4-dimethyl-2,3-

dithiophenyl) nickel tetrabutylammonium, bis(1,2-dithiophenyl) nickel tetrabutylammonium, bis(3,4,5,6-tetrachloro-1,2-dithiophenyl)platinum tetrabutylammonium, bis(1,4-dimethyl-2,3-dithiophenyl)palladium tetrabutylammonium, bis(3,4,6-trichloro-1,2-dithiophenyl)nickel tetra(4-hydroxyl buthyl)ammonium, and the like. The bis(4-diethylaminodithiobenzyl)nickel is known to be a substance which is absorbent of light in the vicinity of about wavelength 1000 nm.

The substrate materials used in the present invention may be those well known to the ordinary worker in this art and may be either transparent or opaque to the laser beam used. However, when writing record is effected from the substrate side with laser beam, the substrate material must be transparent to writing laser beam. On the other hand, when writing record is effected from the side opposite to the substrate, namely from the surface of the recording layer, there is no necessity that the substrate material should be transparent to writing laser beam. However, when reading regeneration is carried out with a transmitted light, the substrate material must be transparent to reading laser beam, while when reading regeneration is carried out with a reflected light, the substrate material may be either transparent or opaque to reading laser beam. Referring to the quality of the substrate material, there may be employed the supports generally used for recording elements made of glass, quartz, ceramics, plastics, paper, plate-like or foil-like metal and the like. Among them, plastics are especially suitable in the points of safety, improved recording sensitivity, flatness, light weight, workability and the like. The typical plastics include vinyl chloride resin, vinyl acetate resin, acrylic resin, methacrylic resin, polyester resin, nitrocellulose, polyethylene resin, polypropylene

resin, polyamide resin, polystyrene resin, polycarbonate resin, epoxy resin and the like.

The recording layer according to the present invention can be formed by the steps of: (1) using a cyanine coloring matter as an essential component or (2) using a cyanine coloring matter and a transition metal complex as essential components and adding thereto a binder and other addition agents in case of necessity, and applying, on a substrate, a solution obtained by dissolving the same in an organic solvent.

In the present invention, however, the recording layer formed of the cyanine coloring matter itself (or only the cyanine coloring matter and transition metal complex) has a sufficient reflectivity. When a binder and other addition agents are added to this recording layer, there is a tendency that the reflective index of the recording layer is deteriorated. Therefore, it is desirable that the recording layer should be formed of the cyanine coloring matter alone or only the cyanine coloring matter and transition metal complex. In this instance, there is no positive necessity of providing a reflective layer, too.

The recording layer used in the present invention can be formed by preparing a solution which has dissolved the essential materials, namely the cyanine coloring matter and the transition metal complex, and together with a binder and/or an addition agent in case of necessity, in an organic solvent and by coating the substrate with the resulting solution.

As the organic solvent there can be used such, for instance, as methanol, methylenedichloride, 1,2-dichloroethane and the like. Coating is carried out in a usual manner such as spraying, roller coating, dipping, rotary coating and the like. Of these coating methods, spinning is most preferable.

As said binder, there can be enumerated polyvinyl butyral, cellulose acetate, polyvinyl acetate, acrylic or methacrylic resin, polyester resin, ethylenevinyl acetate copolymer, polyamide resin or the like, but as described above, it is desirable that such binders should not be used.

As the examples of aforesaid other addition agents (optional components) there can be enumerated a plasticizer, a surface active agent, an antistatic agent, a lubricant, a frame retarder, a stabilizer, a dispersing agent, an antioxidant and the like. When incorporating the transition metal complex in the recording layer, the mixing ratio of the cyanine coloring matter to the transition metal complex is properly in the ratio of 100 wt parts of the former (cyanine coloring matter) to 3 - 60 wt parts of the latter (transition metal complex), preferably 5 - 30 wt parts.

When the optional components have been incorporated in this recording layer, whilst, the amounts of these optional components should be controlled to be under 70 wt % of the total amount of the recording layer.

The cyanine coloring matter and the transition metal complex each may be used singly but two kinds or more may be used concurrently.

In the formation of the recording layer, however, the keenest attention should be paid to the fact that the transition metal complex used herein should be absorbent of the light in the wavelength longer than the wavelength range of which the cyanine coloring matter used herein is absorbent. If this condition is not satisfied, there will be brought about such a disadvantage that the effect of the stability to light radiation given to the cyanine coloring matter is diminished.

The reason why said effect is brought about is not always

clarified, but is considered to consist in that the excited energy of the cyanine coloring matter is received by the transition metal complex and escaped. That is, it may be considered that transfer of said energy is difficult to take place in the transition metal complex which is more absorbent of the short wavelength light than the cyanine coloring matter does.

The thickness of the recording layer is suitably 100 - 1000 Å, preferably 300 - 600 Å, more preferably 300 - 500 Å.

The adhesive layer (undercoat layer), as stated above, is provided between the substrate and the recording layer as occasion demands.

Taking the thermal conductivity into consideration, this adhesive layer may be formed using a heat insulating resin material or an inorganic material in a conventional manner such as vapordeposition coating or the like.

As the resins used herein there can be enumerated vinyl chloride resin, vinyl acetate resin, acrylic or methacrylic resin, polyester such as polyethylene terephthalate, celluloses such as nitro-cellulose, polyamide, polycarbonate, epoxy resin, polyimide, polysulfone, and the like. And, as the inorganic compounds used herein there can be enumerated SiO, SiO_2, TiO_2 and the like. The use of polyimide and polysulfone is particularly preferable. The thickness of the adhesive layer is in the range of about 0.05 to 10 μm, preferably in the range of about 0.1 to 0.5 μm.

The protective layer, as stated above, is formed on the recording layer as occasion demands. This layer may be formed by using the usual method of vapor deposition, coating or the like, and its thickness is suitably in the range of about 0.1 to 10 μm, preferably in the range of about 0.5 to 1.0 μm. The materials used in the formation of the protective layer may be

either organic or inorganic so far as the thin recording layer is protected thereby.

The concrete examples of organic materials are disclosed in Japanese Laid Open Patent Application No. 96716/1974 Specification, Japanese Laid Open Patent Application No. 59626/1976 Specification, Japanese Laid Open Patent Application No. 75523/1976 Specification, Japanese Laid Open Patent Application No. 88024/1976 Specification, Japanese Laid Open Patent Application No. 134633/1976 Specification and the like. Among them, polystyrene, polyethylene terephthalate and ethylene-vinyl acetate copolymer are used profitably. As the concrete examples of inorganic materials, on the other hand, there may be enumerated Al_2O_3, SiO_2, SiO, MgO, ZnO, MgF_2, CuF_2 and the like.

The lasers used in the optical information recording medium according to the present invention include N_2, He-Cd, Ar, He-Ne, ruby, semi-conductor, dye lasers. Among them, the semi-conductor laser is suitable especially from the viewpoints of light weight, easiness of handling, compactness and the like.

Accordingly, information recording is effected by condensing a laser light by means of a lens onto the recording layer to thereby form fine pits thereon, while information reading is effected by radiating a weak laser light onto the recording layer and utilizing the difference in reflection percentage between the pit portions and the other portions.

The recording medium according to the present invention, as is evident from Examples referred to afterwards, is of a superior preservability while maintaining the high sensitivity and the high S/N. The reason why the above mentioned effects of the present invention are brought about has not been investigated minutely yet.

At any rate, the specific coloring matters, in particular the compounds represented by the general formula II are especially superior in the points of thermal resistance and light resistance from among cyanine coloring matters. The above mentioned physical properties of the specified cyanine coloring matters are considered to be influenced by the size of the ionic radius of the counter ion and the electron absorption effect of the halogen on the indole ring.

EXAMPLES

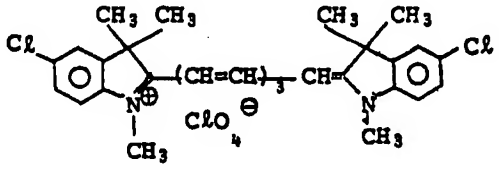
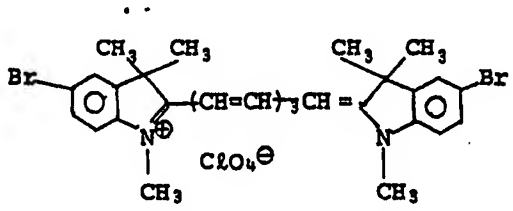
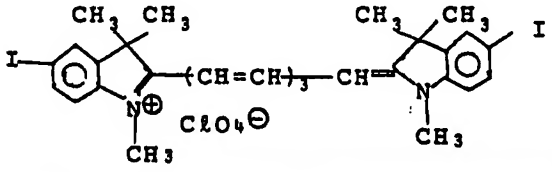
Examples 1-3

An information recording medium was prepared by dissolving each cyanine coloring matter represented by each structural formula in the following Table-1 in a predetermined solvent, applying this solution onto a predetermined substrate (thickness: 1 mm) so as to have a predetermined thickness by means of a rotary coating machine, and drying.

The light resistance life of each of the thus prepared information recording mediums was expressed by a value obtained when said medium was stored at a place where the amount of radiation light is 1/100 of that in the openair, namely a number of years required until the optical density faded to 50 % of the initial value. In the fading test, there was employed the accelerated test method of radiating a tungsten light (54000 lux) under the condition of 35±3°C.

The thermal resistance was measured by acceleration test (120°C), and was expressed in terms of relative thermal deposition ratio. That is, the fading speed of the recording medium measured by acceleration test (120°C) was expressed as the relative value to the fading speed of the recording medium of Example 1 which was estimated at 1.0.

The obtained results were as shown in Table-1.

	Cyanine coloring matter	Solvent	Coloring matter thin film thickness (Å)	Substrate	Spectral characteristics			Light resistance life (year)	Relative thermal decomposition ratio
					λmax (nm) (Solusion)	Thin film (wavelength 800 nm)			
						Absorption rate (%)	Reflection rate (%)		
Example 1		dichloroethane	450	acryl resin	750	56	29	14	1.0
Example 2		ethyl alcohol	400	acryl resin	750	53	30	13	1.15
Example 3		ethyl alcohol	420	polycarbonate resin	750	56	28	13.5	1.15

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Example 4

A dichloroethane solution was prepared which contains 1.25 wt% of the cyanine coloring matter used in Example 1 and 0.05 wt% of bis (4-diethylaminodithiobenzyl, and this solution was applied on a substrate (1 mm-thick acrylic resin plate) by rotary coating to thereby form an about 420 Å - thick recording film. Thus, a recording medium was prepared.

Example 5

A dichloroethane solution was prepared which contains 1.25 wt% of the cyanine coloring matter used in Example 2 and 0.10 wt% of bis(3,4,6-trichloro-1,2-dithiophenyl)nickeltetra(4-hydroxybutyl)ammonium. This solution was applied on a substrate (1 mm-thick glass plate) by rotary coating to thereby form an about 450 Å- thick recording film. Thus, a recording medium was prepared.

Example 6

A dichloroethane solution was prepared which contains 1.25 wt% of the cyanine coloring matter used in Example 3 and 0.20 wt% of bis(3,4,6-trichloro-1,2-dithiophenyl)nickeltetra(4-hydroxybutyl)ammonium. This solution was applied on a substrate (1 mm-thick acrylic resin plate) by rotary coating to thereby form an about 420 Å - thick recording film. Thus, a recording medium was prepared.

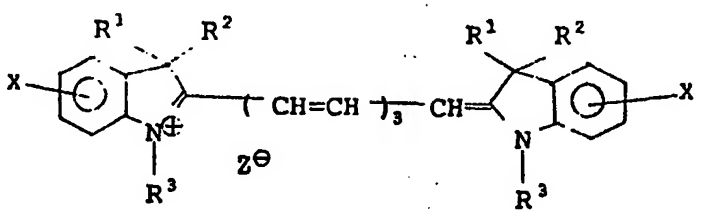
These recording mediums obtained in Examples 4, 5 and 6 were subjected to the same tests as done in Examples 1 - 3. The thus obtained results were obtained as shown in Table-2.

Table 2

	Spectral characteristics			Light resistance life (year)	Relative thermal decomposition ratio
	λmax (nm) (Solusion)	Thin film (wavelength 800 nm)			
		Absorption rate (%)	Reflection rate (%)		
Example 4	750	53	28	31	1.0
Example 5	750	57	30	28	1.15
Example 6	750	56	28	28	1.15

CLAIMS

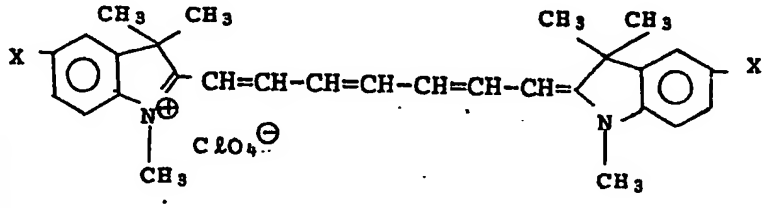
1. An optical information recording medium comprising a substrate and a thin film formed on said substrate, said thin film containing a cyanine coloring matter represented by the following general formula I:



... (I)

(wherein, R^1, R^2 and R^3 may be the same or different and each stands for an alkyl group having 1 - 6 carbon atoms, X stands for halogen, Z stands for a superhalogenic ion, a paratoluene sulfonic ion or an alkylsulfuric ion).

2. A recording medium according to Claim 1 wherein said cyanine coloring matter is the special one represented by the following general formula II:



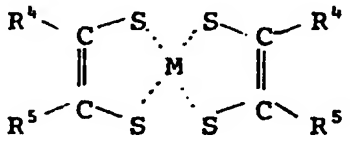
... (II)

(wherein, X stands for one halogen atom selected from the group consisting of fluorine, chlorine, bromine and iodine).

3. A recording medium according to Claim 1 wherein said cyanine coloring matter-containing thin film further contains a transition metal complex which is more absorbent of long wavelength light

than said coloring matter.

4. A recording medium according to Claim 3 wherein said transition metal complex is at least one member of the compounds represented by the following general formula III:



... (III)

(wherein, M is a transition metal selected from nickel, platinum, and palladium, and R^4 and R^5 may be the same or different and each may stand for an alkyl group, a phenyl group, an alkyl-subatituted phenyl group, an alkoxy-substituted phenyl group or a dialkyl-aminophenyl group or R^4 and R^5 may cooperate with each other in forming a ring).

5. A recording medium according to Claim 3 wherein the mixing ratio of the cyanine coloring matter to the transition metal complex is 100 wt parts (the former): 3 - 60 wt parts (the latter).

6. A recording medium according to Claim 1 or Claim 3 wherein said thin film is the one formed by coating.

7. A recording medium according to Claim 1 or Claim 3 wherein said thin film is 100 - 1000 Å in thickness.

8. A recording medium according to Claim 1 or Claim 3 wherein said thin film is 300 - 600 Å in thickness.

9. A recording medium according to Claim 1 or Claim 3 wherein said thin film is 300 - 500 Å in thickness.

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European Patent Office

EUROPEAN SEARCH REPORT

Application number

EP 84 11 0819

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
A	PATENT ABSTRACTS OF JAPAN, vol. 8, no. 195, 7th September 1984, page (M-323) (1632); & JP-A-59-83695 (TDK K.K.) 15-05-1984	1,4	G 11 B 7/24 C 09 B 23/08
A	PATENT ABSTRACTS OF JAPAN, vol. 8, no. 174, 10th August 1984, page (M-316) (1611); & JP-A-59-67092 (TDK K.K.) 16-04-1984	1	
A	US-A-4 219 826 (A. BLOOM et al.) * Claims 1,6 *	4	
A	PATENT ABSTRACTS OF JAPAN, vol. 8, no. 12, 19th January 1984, page (M-269) (1449); & JP-A-58-175693 (RICOH K.K.) 14-10-1983	4	TECHNICAL FIELDS SEARCHED (Int. Cl.4) C 09 B 23/00 G 03 C 1/00 G 11 B 7/00
A	DE-A-2 543 092 (AGFA-GEVAERT AG) * Claim 9 *		
A	DE-C- 499 967 (I.G. FARBENINDUSTRIE AG)		

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
BERLIN	07-05-1985	HASS C V F

CATEGORY OF CITED DOCUMENTS

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